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Ambient Volatile Organic Compounds in a Suburban Site between Beijing and Tianjin: Concentration Levels, Source Apportionment and Health Risk Assessment

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Abstract

Volatile organic compounds (VOCs) have vital implications for secondary pollutants, atmospheric oxidation and human health. Ambient VOCs were investigated using an online system, gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID), at a suburban site in Xianghe in the North China Plain from 6 November 2017 to 29 January 2018. Positive matrix factorization (PMF) receptor model was applied to identify the major VOC contributing sources. Four-step health risk assessment method was used to estimate risks of all risk-posing VOC species. A total of 101 VOCs were quantified, and the mean concentration of total VOCs was 61.04±65.18 ppbv. The VOCs were dominated by alkanes (38.76%), followed by alkenes, aromatics, halocarbons, OVOCs, acetylene and acetonitrile. The results of PMF revealed that vehicle exhaust, industrial emissions, liquefied petroleum gas & natural gas, solvent utilization and secondary and long-lived species contributed 31.0%, 26.4%, 18.6%, 13.6% and 10.4%, respectively, to the total VOCs. Pollutant-specific and source-specific noncarcinogenic and carcinogenic risk estimates were conducted, which showed that acrolein and vehicle exhaust had evident noncarcinogenic risks of 4.9 and 0.9, respectively. The carcinogenic risks of specific species (1,3-butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane) and identified sources were above the United States Environmental Protection Agency (USEPA) acceptable level (1.0×10^{-6}) but below the tolerable risk level (1.0×10^{-4}). Vehicle exhaust was the largest contributor (56.2%) to noncarcinogenic risk, but solvent utilization (32.6%) to carcinogenic risk. Moreover, with the evolution of pollution levels, almost all VOC species, contributions of alkenes, aromatics, solvent utilization and vehicle exhaust, and pollutant-specific and source-specific risks increased continuously and noticeably. Collectively, our findings unraveled the importance of alkenes, aromatics, solvent utilization and vehicle exhaust

in the evolution of pollution levels. Future studies should consider targeting these VOC groups and sources when focusing on effective reduction strategies and assessing public health risks.

Keywords: VOCs; source apportionment; health risk assessment; vehicle exhaust; solvent utilization

1 Introduction

Overwhelming quantities of VOCs are emitted into the troposphere from anthropogenic sources and biogenic sources (Chen et al., 2019; Li et al., 2019b). VOCs are not merely critical precursors to ground-level ozone (O_3), secondary organic aerosol (SOA), peroxyacetyl nitrate (PAN) and polycyclic aromatic hydrocarbons (PAHs), which have a strong influence on the oxidation capacity of the troposphere (Gentner et al., 2017; McDonald et al., 2018), but are unequivocally harmful to human health and are occurring in close proximity to populated areas (Bolden et al., 2015). For instance, benzene, the simplest aromatic VOC, is listed as a toxic air contaminant under the USA Clean Air Act (CAA) in section 112 (https://www3.epa.gov/airtoxics/orig189.html) and is even classified as a known human carcinogen (IARC Group 1[1]) by the International Agency for Research on Cancer (IARC). Chronic exposure to elevated levels of benzene can reduce the production of both red and white blood cells from bone marrow in humans, resulting in aplastic anaemia (http://www.inchem.org/documents/ehc/ehc/ehc150.htm). Epidemiological studies have shown that toluene (IARC Group 3), ethylbenzene (IARC Group 2B) and xylenes (IARC Group 3) could increase the odds of low birth weight, rhinitis and cardiovascular disease (Bolden et al., 2015; Halliday et al., 2016). Consequently, vast multitudes of studies on VOCs are being conducted globally, covering measurement techniques (Wang et al., 2014; Bourtsoukidis et al., 2017), chemical mechanisms (Atkinson and Arey, 2003; Atkinson et al., 2006), reactivity scales (Carter, 1994; Derwent et al., 1998), emission inventories (Bo et al., 2008; Huang et al., 2011; Wu and Xie, 2017; Zhao et al., 2017; Zhou et al., 2017), health risk assessment (Li et al., 2014b; Bari and Kindzierski, 2017) and removal technology (Domeno et al., 2010; Sui et al., 2016; Wolowiec et al., 2017).

[1] Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable in terms of its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans.

Rising anthropogenic interferences due to astonishing economic growth and rapid industrialization and urbanization in China have triggered a dramatic increase in VOCs since the Chinese Economic Reform began in 1978 (Wu and Xie, 2017), particularly in some highly industrialized and densely populated regions, e.g., North China Plain (NCP) (Li et al., 2015b; Qi et al., 2017), Yangtze River Delta (YRD) (Shao et al., 2016; Xu et al., 2017), Pearl River Delta (PRD) (Lu et al., 2013; Ou et al., 2015) and Sichuan Basin (SB) regions (Li et al., 2014a). Over the past several decades, the abundance and speciation of VOCs, source apportionment of VOCs and the relationship of VOCs with O_3 and SOA in NCP, which are mainly concentrated in the megacities of Beijing and Tianjin, have been comprehensively studied (Guo et al., 2017). The common findings in the NCP region were that alkanes and aromatics were the most abundant VOCs (Duan et al., 2008; Wang et al., 2015); vehicle-related emissions were the most predominant contributor to VOCs (Song et al., 2007; Shao et al., 2009); the photochemical O_3 formation in Beijing was VOC-limited (Guo et al., 2017). To tackle the problem of severe air pollution, China has implemented active clean air policies in recent years. As a consequence, the emissions of major air pollutants have decreased during 2010–2017 as follows: -62% for SO_2, -17% for NO_x, -27% for CO, -38% for PM_{10}, -35% for $PM_{2.5}$, -27% for BC and -35% for OC (Zheng et al., 2018). However, nonmethane volatile organic compounds (NMVOCs) emissions are estimated to have increased by 11% because China lacked effective emission control measures on NMVOCs (Zheng et al., 2018).

The average annual concentrations of PM_{10}, $PM_{2.5}$, SO_2, NO_2 and CO in Langfang in 2017 (http://www.lfhbj.gov.cn/) were 102, 60, 14, 48 and 2900 ug/m^3, dropping 8.93%, 9.09%, 22.22%, 7.69% and 17.14%, respectively, compared with 2016. These official statistics showed that the air quality has substantially improved in Langfang. However, relatively few research studies

109 concerning the current situation of VOCs pollution in Xianghe have been completed (Xin et al.,
110 2015; Li and Lu, 2017). Limited available studies have mainly focused on the determination of the
111 concentration levels and seasonal variation of VOCs. For example, the study conducted from 12
112 September to 10 October 2012, in which 56 VOCs were measured, reported that the average
113 concentration of total VOCs in Xianghe was 28.2 ppbv with the highest concentration being 79.4
114 ppbv in April and the lowest being 5.8 ppbv in August, and aromatics were the highest abundant,
115 accounting for 37.1%, followed by halocarbons (30.2%), alkanes (26.8%), and alkenes (10.5%)
116 (Xin et al., 2015). These measurements provided the first snapshot of VOC concentrations in
117 Xianghe. However, field measurements online of VOCs in Xianghe remain scarce. To further
118 advanced our understanding of VOCs pollution, more measurements of ambient VOCs in Xianghe
119 are still needed.

120 In this study, a three-month campaign was carried out at Xianghe, a typical suburban site
121 located between the megacities of Beijing and Tianjin from 6 November 2017 to 29 January 2018.
122 Continuous measure atmospheric VOCs was made using an electronic cryogenic technology for
123 preconcentration and a GC-FID/MS for separation and detection. The objectives of the present study
124 are to (1) determine the ambient VOC pollution level, (2) identify and apportion the major sources,
125 and (3) screen the human health risk assessment of risk-posing VOC species and sources. To our
126 knowledge, this study represents the first online field observations of VOCs in Xianghe. The data
127 collected here are unique and valuable. The results from this work can provide useful information
128 for policy-makers to develop strategies to alleviate air contamination in Xianghe.

2 Methodology

2.1 Sampling-site description

The sampling site is located at the Xianghe Atmospheric Observatory (39.798°N, 116.958°E; 15m above sea level). The sampling site is a typical suburban site in the serious pollution region, the Beijing–Tianjin–Hebei large urban region, which is approximately 50 km southeast of Beijing, 75 km northwest of Tianjin, and 35 km northeast of Langfang in Hebei province. The unique geographical location makes it an indispensable platform in Beijing air pollution warning system and plays an important strategic role in regional air pollution research. The sampling site is approximately 4 km west of the downtown center and is surrounded by residential areas and agricultural land (see Figure 1).

2.2 VOCs Measurements

Ambient VOC samples were analyzed with a time resolution of 1 h using a custom-built gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID). A complete analysis cycle for ambient VOC measurements by the online GC-MS/FID system includes five stages: preparation, sampling and preconcentration, injection/GC analysis, idle/GC analysis, and back purge/GC analysis (Wang et al., 2014). In the preparation stage, air samples were vented from the sampling and pre-concentration system via the pump, which could reduce or avoid interferences by previous samples. In addition, temperatures for H_2O and enrichment traps during the preparation stage were set at their corresponding values for the sampling and pre-concentration stage. In the sampling and preconcentration stage, air samples were drawn into the FID channel and MS channel for VOCs enrichment. The temperatures of the enrichment traps for both channels were set at -150℃. In the injection/GC-analysis stage, The concentrated VOCs in the enrichment traps were

volatilized by thermal desorption at 110℃ and were injected into the GC system by Helium carrier gas. After the 1 minute injection, GC analysis was continued for VOCs separation and detection. Moreover, the sampling and pre-concentration system shifted to the idle condition. Twenty minutes after the injection/GC-analysis stage, a 5 minutes back purge for the sampling and pre-concentration system was programmed for removing residues in the water management traps and cleaning sampling lines to prevent samples carryover effects. Briefly, samples are collected into GC-MS/FID for 5 min every 1 h at a flow of 60 mL min^{-1}. Both the CO_2 and H_2O were removed in an electronic cryogenic pre-concentrator (TH300, Wuhan Tianhong Environmental protection industry co., LTD, Wuhan, China) before VOC analysis. The air was then thermally desorbed at 100 °C and transferred for analysis in a gas chromatography (GC, 7820A, Agilent Technologies, Santa Clara, CA, USA) coupled with mass spectrometric detector (MSD)/flame ionization detector (FID) (5977E, Agilent Technology, Santa Clara, CA, USA). Dual columns and detectors were applied for the simultaneous analysis of C2-C12 hydrocarbons. C2-C5 hydrocarbons were separated on a PLOT-Al_2O_3 column (15 m×0.32 mm ID×3 μm, J&W Scientific, USA) and were measured by the FID channel. Other compounds were separated on a semipolar column (DB624, 60 m×0.25 mm ID×1.4 μm, J&W Scientific, USA) and were quantified using a quadrupole MS detector. The VOC species measured by GC-MS/FID are listed in Table S1. Several OVOCs species are also measured by the MS channel, including acetaldehyde, acrolein, acetone, propanal, methyl tert-butyl ether (MTBE), n-butanal, methyl ethyl ketone (MEK), methyl vinyl ketone (MVK), methacrolein (MACR), 2-pentanone, pentanal, 3-pentanone and hexanal. Good agreements were found between GC-MS/FID and high-sensitivity proton-transfer-reaction mass spectrometry (PTR-MS) for C3-C4 carbonyls and MVK+MACR, with correlation coefficients larger than 0.90 and slopes ranging from 0.7 to 1.4

(Yuan et al., 2012; Chen et al., 2014; Wang et al., 2014). The GC was programmed for a 35 min run time, with a temperature program as follows: staying in 35°C for 3 minutes, then rising to 180°C at a heating rate of 6°C min^{-1} and keeping it for 5 minutes, then rising to 185°C at a heating rate of 6°C min^{-1} and keeping it for 2 minutes. The MSD was operated with the electron ionization (EI) impact (70 eV), where the ions were detected in the selected ion monitoring (SIM) mode with a minimum of two and maximum of eleven ions being monitored for each time window.

The analyzed compounds were subjected to rigorous quality assurance and quality control procedures (QA/QC). The VOCs detected by FID were quantified by the external standard method, and the components detected by MS were quantified by the internal standard method. Four compounds, i.e., bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and bromofluorobenzene, were used as internal standards (Li et al., 2015a). Specifically, the system was calibrated at multiple concentrations in the range of 0.8-8 ppbv by two gas standards, i.e., a mixture of 57 PAMS (provided by Spectra Gases Inc., USA), and a mixture of oxygenated VOCs (OVOCs) and halocarbons (provided by Spectra Gases Inc., USA). Daily calibrations were performed every day, and the variations of target species responses were required to be within ±20% from the calibration curve. R^2 values for calibration curves ranged from 0.941 (n-dodecane) to 1.000 for VOCs, indicating that integral areas of peaks were proportional to the concentrations of target compounds. The method detection limit (MDL) of the online GC-FID/MS system for all measured compounds ranged from 0.003 to 0.092 ppbv and the relative standard deviation (RSD) for measured compounds ranged from 2.1% to 14.9% (Table S1). To check the stability of the instrument, routine calibration was operated periodically, by using a calibration gas with a mixing ratio of 2 ppbv and consisting of 56 kinds of VOC components. The variations between measured

and nominal concentrations of the periodically calibration was within 10%. The signal variations of each targeted compound due to system instability were corrected by the signal of CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) due to its long atmospheric lifetime and quite stable anthropogenic emissions (Yuan et al., 2013; Chen et al., 2014).

2.3 Source apportionment: PMF model analysis

US PMF 5.0 (U.S. EPA, 2014) was comprehensively applied to identify the initial contribution of sources to samples based on the composition or fingerprints of the sources. The method is described in greater detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997) and reviewed briefly here. The PMF is a multivariate factor analytical tool that decomposes the speciated measurement data matrix x of i by j dimensions into two matrices-factor profiles (f) and factor contributions (g):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

where p is the total number of independent sources, g_{ik} stands for the contribution of k^{th} factor in the i^{th} sample, f_{kj} is the load of j^{th} compound in the k^{th} source and e_{ij} is the relevant residual for each sample/species. Factor contributions and profiles are derived by the PMF model minimizing the objective function Q:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{\sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right] \quad (2)$$

where m and n are the numbers of samples and chemical species, respectively, u represents the uncertainty of each data. The theoretical Q ($Q_{theoretical}$) can be calculated as Eq. (3), and the best PMF solution should have $Q/Q_{theoretical}$ with the value of~1.

$$Q_{theoretical} = i \times j - p \times (i + j) \quad (3)$$

Two files including species concentrations and uncertainty file are required to be introduced into the EPA PMF 5.0 model. The concentrations file is a matrix (X matrix) of number of samples (column) plus the number of species (row), i.e., 2040×49 in this study. PMF analysis requires a complete data set; in order to reduce the error, the samples with missing values for individual species were excluded rather than replaced by the mean concentrations of the remaining observations (Huang et al., 2017). The equation-based uncertainty dataset is constructed according to the method detection limit (MDL) and error fraction (%). If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using a fixed fraction of the MDL, as Uncertainty=5/6×MDL. If the concentration is greater than the provided MDL, the calculation is defined as $\text{Uncertainty} = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (0.5 \times \text{MDL})^2}$. Not all 101 measured VOCs are introduced into the PMF model, there are some rules to decide which species should be included or excluded from the PMF model: 1) the chosen species had relatively high concentrations (i.e., ethane, ethylene and propane, the top three species in this study) and/or were typical tracers for specific emissions (i.e., acetylene is marker of combustion sources); 2) highly collinear species, such as iso-butane & n-butane, iso-pentane& iso-pentane, benzene & toluene, m/p-Xylene & o-Xylene are included (Figure S1); 3) species that are highly reactive are excluded, except for the source markers, since they are rapidly reacted away in the ambient atmosphere (Shao et al., 2016; Zheng et al., 2017; Li et al., 2019a); 4) species were incorporated in PMF analysis based on their potential toxicity (e.g., 1,3-butadiene, tetrachloroethylene, bromoform). Finally, a total of 48 species, including 9 alkanes, 5 alkenes, 7 OVOCs, 10 aromatics and 15 halocarbons, acetylene and acetonitrile were selected for the input data. In addition, the total measured VOC was included as an input variable in the PMF model to directly obtain source contribution instead of using post-hoc regression analysis in this

study. Prior to the PMF model run, the retained species are firstly classified into strong, weak, and bad based on their signal-noise-ratios (S/N). Species with S/N ratios less than 0.5 are grouped into bad and into weak if S/N ratios are in the range of 0.5-1.0 (US EPA, 2014). Finally, 41 species were categorized as strong and seven species (bromomethane, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, 1,2-Dibromoethane, bromoform, 1,1,2,2-Tertrachloroethane and 1,4-Dichlorobenzene) were characterized as weak. Choosing the optimal number of factors in modeling is a critical question. Too many factors will result in meaningless factor profiles, while too few factors will make it difficult to segregate the mixing sources (Bressi et al., 2014; Zheng et al., 2017). The Q-values, source profiles and scaled residuals distributions were examined to obtain the most reasonable factor solutions (Ji et al., 2018; Li et al., 2019a). The uncertainties of the results were assessed by bootstrapping (BS) and displacement (DISP) (Belis et al., 2015; Brown et al., 2015; Debevec et al., 2017). The detailed information as to how to find the optimum factor solutions and the uncertainty estimation are described in the Supplementary material.

Significantly, previous studies have shown that the emissions from biogenic emissions are very limited in wintertime because emission from biogenic sources, eg., isoprene, the most abundant compound from biogenic emissions, is sensitive to a number of environmental parameters, especially temperature and light intensity (Guenther et al., 1993; Pacifico et al., 2009; Ding et al., 2014; Saunier et al., 2017). A latest source apportionment study conducted at the atmospheric monitoring site in the northeast of Langfang city from April 2016 to March 2017 revealed that the contributions of biogenic emission contributed to ambient VOCs in November, December and January were only 0.7%, 0.8% and 2.3%, respectively (Song et al., 2019). In addition, in this study, the linear correlation between isoprene and temperature was extremely poor, fairly correlations

between isoprene and three short-lived unsaturated hydrocarbons, i.e., 1,3-butadiene, trans-2-butene and propylene, as showed in Figure S2, which is partial evidence that isoprene produced from local vehicular exhaust may be responsible for wintertime isoprene mixing ratio at Xianghe. Therefore, this study only focused on the source characteristics of anthropogenic emissions.

2.4 Human health risk assessment of VOCs species and sources

A screening-level health risk assessment is the process to characterize the nature and magnitude of health risks to humans and ecological receptors from chemical contaminants and other stressors that may be present in the environment (https://www.epa.gov/risk). To assess public health risks associated with chronic inhalation exposure, a four-step health risk assessment method proposed by the U.S. National Academy of Sciences has become an internationally recognized health risk assessment method and has been used in several studies to screen ambient concentrations of hazardous air pollutants (Bari et al., 2016; Bari and Kindzierski, 2017, 2018).

The USEPA's risk assessment methods are generally used in studies to evaluate carcinogenic and non-carcinogenic risks of pollutant-specific (Li et al., 2014b; Zhang et al., 2017). However, pollutant-specific risk estimates may provide limited information for air quality management due to contributions of multiple sources to each compound. Source-specific risk estimates may add valuable information for understanding potential control strategies for particular sources (Bari and Kindzierski, 2018). Source-risk apportionment, which is a combination of risk assessment and receptor modeling using actual measurements, has been applied in several studies worldwide to determine relative source contributions to human health risks (Wu et al., 2009; Liao et al., 2015; Bari and Kindzierski, 2017).

In this study, out of all detected species, only 31 VOC species with known toxicity values were

282 considered, including 27 noncarcinogenic species and 13 carcinogenic species. Target VOCs and
283 associated toxicity values of health risk assessment can be found in Table S2. Carcinogenic and non-
284 carcinogenic risks of all risk-posing VOC species were evaluated using the EPA inhalation unit risk
285 (IUR, μg m^{-3}) and reference concentrations (RfCs, mg m^{-3}) associated with the exposure
286 concentration (EC) based on the investigation of the Chinese behavior pattern for each trace element.
287 Noncarcinogenic and carcinogenic risk from inhalation exposure to the i^{th} source was estimated as
288 the sum of cancer and noncancer risks of all available n risk-posing VOC species in PMF-derived
289 profiles. Detail information on the health risk estimate procedures are presented in the
290 Supplementary material.

291 **3 Results and discussion**

292 **3.1 Overall concentration characteristics of VOCs**

293 In this study, we identified and quantified approximately 101 VOCs from C2 to C12, including
294 29 alkanes, 11 alkenes, 13 OVOCs, 16 aromatics, 30 halocarbons, acetylene and acetonitrile, as
295 presented in Table S1. The time series and fractions of the hourly VOC category concentrations
296 determined by GC-FID/MS from 6 November 2017 to 29 January 2018 are presented in Figure 2.
297 The gaps in the data were due to maintenance and calibration of GC-FID/MS or power failure.

298 Over the entire period of the study, the mean concentration of total VOCs was 61.04±65.18
299 ppbv. Taking the study period as a whole, it was observed that the average composition of VOCs
300 was mainly characterized by alkanes (23.66±23.90 ppbv; 38.76% of the total VOCs), followed by
301 alkenes (12.27±16.47 ppbv; 20.10%), aromatics (8.27±10.30 ppbv; 13.55%), halocarbons
302 (8.47±9.52 ppbv; 11.62%) and OVOCs (5.18±4.80 ppbv; 8.49%) and to a lesser extent by acetylene
303 (4.24±5.20 ppbv; 6.95%) and acetonitrile (0.32±0.84 ppbv; 0.53%)，as presented in Figure 2.

Alkanes were dominated by a strong presence of ethane (9.60±10.08 ppbv), propane (5.07±5.71 ppbv), n-butane (2.63±3.27 ppbv), iso-butane (1.49±1.75 ppbv) and iso-pentane (1.02±1.22 ppbv), representing 93.07% of the alkanes. Approximately 90.82% of the alkenes were mainly characterized by ethylene, propylene and 1-butene, with corresponding average mixing ratios of 8.73±11.73, 2.02±2.99 and 0.39±0.77 ppbv, respectively. M/p-xylene (1.99±2.83 ppbv), benzene (1.98±2.72 ppbv), toluene (1.91±2.35 ppbv), ethylbenzene (0.74±1.09 ppbv) and o-xylene (0.67±1.00 ppbv), collectively called BTEX, together contributed to 88.10% of the aromatics. The top five halocarbon species were methylene chloride (2.71±5.61 ppbv), 1,2-dichloroethane (1.55±2.71 ppbv), chloromethane (0.69±0.56 ppbv), chloroform (0.68±1.27 ppbv) and 1,2-dichloropropane (0.61±1.42 ppbv). These five species accounted for 87.98% of the halocarbons. Among the OVOCs, acetone and acetaldehyde were the two most abundant species with average mixing ratios of 1.79±1.83 ppbv and 1.53±1.49 ppbv, respectively. The top ten VOCs measured in this study are presented in Figure S3 and Table S3 for comparison with those from cities in China. In general, the average concentrations of the top ten VOCs fell within the ranges reported for other Chinese cities (Geng et al., 2010; Guo et al., 2011; An et al., 2014; Zou et al., 2015; Liu et al., 2016a; Wu et al., 2016; Liu et al., 2017). During the entire sampling period, the average concentrations of the top ten VOCs in winter in Xianghe were remarkably greater than those reported in fall in Beijing (Wu et al., 2016) but comparable with those observed in winter in Beijing (Liu et al., 2017). The discrepancies in the VOC average concentrations can be explained by the strong intensity of pollution emissions and the fluctuations in meteorological conditions, such as wind speed, relative humidity, air temperature and pressure, atmospheric stability, the height of the planetary boundary layer, and air mass origins (Song et al., 2018; Yang et al., 2018; Zheng et al., 2018; Li et al., 2019a).

3.2 Source profiles and apportionments of VOCs

In this campaign, a solution of five factors was chosen to best represent VOCsources at Xianghe from 6 November 2017 to 29 January 2018. Figure 3 presents the source profiles i.e., chemical composition of emission sources of each of the identified source factors from the base runs and the average contributions (in ppbv and percentage) of PMF-derived sources to ambient VOCs. The regression relationship between modeled and measured total VOCs concentrations (Figure S4) showed a good fit with square of the correlation coefficient (R^2) of 0.97 suggesting that statistically, observed VOC concentrations at Xianghe were well represented by the PMF model-resolved source factors. Bootstrapping mapping of PMF factor solutions are shown in Table S4, indicating the results were more stable with all factors mapped in BS in 100%, and there are no unmapped BS factors and no swaps with DISP. In order to further determine if source contributions are really different, we summary the error estimation of concentrations and percentages for TVOCs, as showed in Table S5. For each factor, the median bootstrap value is typically within ±5% of the base run value and the interquartile range of the bootstrap run values is mostly within ±5% of the bootstrap median, except for industrial emissions where the interquartile range of the bootstrap run values is 22.7% of the bootstrap median, showing that the percentages were reasonable. The presences of discrepancies of the concentrations/percentages of base value, BS 5th, BS 25th, BS 50th, BS 75th and BS 95th among factors, as showed in Table S5, demonstrate that these contributions are really different. In conclusion, the analysis of uncertainty revealed that the identified source profiles are reasonable in this study.

Factor 1 was characterized by 82.4% of the total 1,4-Dichlorobenzene mixing ratios, 81.8% of the total bromoform mixing ratios, 79.7% of the total 1,1,1-Trichloroethane mixing ratios and 73.6%

of the total carbontetrachloride mixing ratios, which have a long lifespan in the atmosphere (Mccarthy et al., 2007; Li et al., 2015a). Factor 1 also included high mixing ratios of pentanal (72.7%) and hexanal (68.5%). Based on the abundances of long-lived compounds and carbonyls, factor 2 was assigned to secondary and long-lived species, and its contribution to the observed VOCs was 10.4%. Previous studies also reported that secondary formation was still an important source of carbonyls, although carbonyls mainly came from direct anthropogenic emissions in winter (Chen et al., 2014; Li et al., 2015a). Factor 2 consisted of abundant 2-methylhexane, cyclohexane and n-hexane, which are widely used solvents and adhesives in paints (Cai et al., 2010). The loadings of aromatics, including o-xylene, m/p-xylene and ethylbenzene , were high, accounting for 68.1% of o-xylene, 66.8% of m/p-xylene, 62.7% of ethylbenzene, respectively, in the atmosphere; these species are the dominant components of organic paint solvents (Ying et al., 2008; Li et al., 2015a; He et al., 2019). Consequently, we believe that the loadings of VOC species in this source were related to solvent utilization, which contributed 13.6% of the observed VOCs. Factor 3 accounted for 26.4% of the total observed VOCs and for more than 91.7% of our measured 1-pentene, which is often considered as a tracer for industrial emissions (Gao et al., 2014), so we attributed this factor to industrial emissions. Factor 4 was abundant in 1,3-butadiene, propylene, ethylene and benzene, which accounted for 78.3%, 68.7%, 68.3% and 61.4% of the total 1,3-butadiene, propylene, ethylene and benzene, respectively. These chemicals are typical VOCs observed in vehicle exhaust (Ying et al., 2008; Chen et al., 2014; Jun-Lin et al., 2014; Song et al., 2018), suggesting that this factor was associated with vehicle exhaust and was responsible for 31.0% of the total VOCs. Factor 5 contributed 63.1% of measured n-butane, 62.3% of measured n-pentane, 61.8% of measured iso-butane, 58.1% of measured iso-pentane, 40.0% of measured MTBE and 38.1% of measured propane.

It has been reported that these chemicals are representative species in liquefied petroleum gas & natural gas (Wang et al., 2015; Li et al., 2019a). Totally, 18.6% of the observed VOCs were associated with liquefied petroleum gas & natural gas.

The source apportionment results showed that the dominant source in this study was vehicle exhaust (18.7 ppbv, 31.0%), followed by industrial sources (15.9 ppbv, 26.4%), liquefied petroleum gas & natural gas (11.2 ppbv, 18.6%), solvent utilization (8.2 ppbv, 13.6%) and secondary and long-lived species (6.3 ppbv, 10.4%). Comparable results can be found in latest source apportionment study conducted at the atmospheric monitoring site in the northeast of Langfang city (Xianghe city belong to Langfang district) from April 2016 to March 2017 (Song et al., 2019). The source apportionment results in this study were compared with former studies, as listed in Table S6. In these studies, vehicle exhaust was the major source in urban and industrial areas, contributing approximately 27.8-58.3% to the total VOCs. Among the compared Chinese cities, the contribution of vehicle exhaust in this study was lower than that in other cities due to the huge vehicle flows in megacities. The contribution of industrial emissions in this study was higher than the values reported for various Chinese cities. The contribution of liquefied petroleum gas & natural gas was comparable with that in Tianjin, Hong Kong and Wuhan but much lower than that in the Junggar Basin. Given that there are no LPG-fueled vehicles in Xianghe, the emissions of LPG-related VOCs from household and catering were considerable. The contribution of solvent utilization to VOCs in Xianghe is higher than that in Tianjin (Liu et al., 2016b), , lower than that in Lanzhou, Wuhan, Baoji, Chengdu, Nanjing and Hong Kong (Guo et al., 2004; Gao et al., 2014; Jia et al., 2016; Lyu et al., 2016; Xue et al., 2017; Song et al., 2018), and comparable with that in Beijing (Li et al., 2015a). The contribution of secondary and long-lived species was much higher than that in Beijing.

392 Nevertheless, source identification and source contributions strongly depend upon the model, the
393 study period, and the species and profiles used for source apportionment (Pandolfi et al., 2008; Yuan
394 et al., 2012; Lyu et al., 2016). In summary, the comparison suggests a general characteristic of source
395 apportionments of VOCs, where vehicle-related emissions, industrial sources and solvent utilization
396 were the major contributors to ambient VOCs.

397 **3.3 Pollutant- and source-specific health risk assessment**

398 The HQs and carcinogenic risks of hazardous VOC species via inhalation exposure in the
399 present study and in other cities in China were estimated and are presented in Figure 4 and listed in
400 Table S7. Apart from benzene, o-xylene, bromomethane, trichloroethylene and 1,4-dichlorobenzene,
401 the HQ of other noncarcinogens was higher than that in Beijing (Zhang et al., 2017). With the
402 exception of styrene, the HQ of other aromatics was basically within the values reported for other
403 Chinese cities (Cai et al., 2010; Li et al., 2013; Zhang et al., 2017), as showed in Figure 4a. A
404 noncarcinogenic risk is represented by hazard index (HI). US EPA states that if HI <1, there is no
405 appreciable risk of adverse health effects, while HI >1 indicates a chance of noncancer effects
406 occurring (USEPA, 2009). In our study, HI of the observed noncarcinogenic species was 5.2, so they
407 had significant non-carcinogenic risk. Specifically, among the noncarcinogens, only the HQ of
408 acrolein (4.9) exceeded the value of 1, indicating a obvious noncarcinogenic risk. In contrast, the
409 HI of other noncarcinogens was lower than the value of 1, suggesting no chance of noncancer effects
410 occurring.

411 Among the carcinogens, as illustrated in Figure 4b and Table S7, with the exception of benzene,
412 trichloroethylene, tetrachloroethylene and vinylchloride, the carcinogenic risks of the four other
413 carcinogens in this study were evidently greater than those reported in Beijing (Zhang et al., 2017).

414 The excess cancer risk range recommended by the (USEPA, 2009) for public health protection is
415 one in a million (1.0×10^{-6}) acceptable risk level to one in ten thousand (1.0×10^{-4}) tolerable risk level.
416 The carcinogenic risks of 1,3-butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane
417 were above the acceptable level of 1.0×10^{-6} but below a tolerable risk of 1.0×10^{-4}, showing a
418 potential carcinogenic risk (Dutta et al., 2009; Zhang et al., 2012). The cancer risks of other VOC
419 species were below the acceptable level of 1.0×10^{-6}, which means that there might be no obvious
420 cancer risk from these VOC species. In this study, the average cumulative carcinogenic risk (the
421 summation of available individual compound risks) based on personal exposure was 5.4×10^{-5}.
422 Compared with other studies using the same IURs, cumulative carcinogenic risks for personal
423 exposure were higher than average estimates in Tianjin (3.0×10^{-5}) (Zhou et al., 2011) and South
424 Baltimore (4.3×10^{-5}) (Payne-Sturges et al., 2004). The difference in the cumulative cancer risk
425 among these studies may be the result of VOCs species and individual activities magnifying the
426 variability in personal exposure concentrations (Payne-Sturges et al., 2004; Zhou et al., 2011), eg.,
427 13 VOCs in this stuy, but 9 VOCs in Payne-Sturges' study and 5 VOCs in Zhou's study. In short,
428 from pollutant-specific health risk perspective, much more attention should be paid to acrolein, 1,3-
429 butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane.
430 In addition, health risk was apportioned to the five identified sources by summing the
431 carcinogenic and noncarcinogenic risks of all available risk-posing VOC species in a particular
432 source (Bari and Kindzierski, 2017, 2018). The source-specific noncarcinogenic and carcinogenic
433 risk values are shown in Figure 5a-5b and Table S8. Noncarcinogenic risks of different sources
434 ranged from 0.01 (solvent utilization) to 0.9 (vehicle exhaust), and all noncarcinogenic values were
435 lower than the USEPA safe level (1.0), except for vehicle exhaust, where the noncarcinogenic value

436 was comparable with the safe level, as illustrated in Figure 5a. The source-specific carcinogenic risk
437 of different sources ranged from 1.0×10^{-6} (secondary and long-lived species) to 3.1×10^{-6} (solvent
438 utilization), and all risk values were above the USEPA acceptable level (1.0×10^{-6}) but below the
439 tolerable risk (1.0×10^{-4}). In general, vehicle exhaust posed the greatest noncarcinogenic risk to
440 public health (56.2%), followed by secondary and long-lived species (23.1%), industrial emissions
441 (17.7%) and liquefied petroleum gas & natural gas (2.2%). Solvent utilization posed a relatively
442 low noncarcinogenic risk (0.8%) to public health. Solvent utilization was the largest contributor
443 (32.6%) to carcinogenic risk, followed by vehicle exhaust (30.3%), industrial emissions (15.0%)
444 and Liquefied petroleum gas & natural gas (11.5%). Secondary and long-lived species posed a
445 relatively low carcinogenic risk (10.6%) to public health, as depicted in Figure 5b. In brief, from
446 source-specific health risk perspective, much more attention should be paid to vehicle exhaust and
447 solvent utilization.

448 It should be mentioned that there are some limitations to our health risk assessment.
449 Noncarcinogenic and carcinogenic risks were calculated based solely on 27 and 13 detected
450 hazardous VOCs, respectively, whereas other potentially important hazardous VOCs, for example,
451 formaldehyde, acetophenone, and cresols/cresylic acid, in the USEPA list of 187 air toxins
452 (https://www3.epa.gov/airtoxics/orig189.html) and 30 urban air toxins (https://www.epa.gov/urban-
453 air-toxics/urban-air-toxic-pollutants) were not measured in this study. It is reported that
454 formaldehyde and BTEX are more serious indoors than outdoors (Wang et al., 2007), and according
455 to the exposure parameters of the Chinese population, the Chinese population spends most of their
456 day indoors (1213 min/day); hence, the estimations can only represent the lower limits. Overall, the
457 resultant inhalation noncarcinogenic and carcinogenic risks estimated here are a reasonable first step

458 for understanding ambient VOC risks to public health in Xianghe.

459 **3.4 Evolution at different pollution levels**

460 Theoretically, determining high and low pollution levels from total VOCs concentrations are
461 more common and reasonable than that from $PM_{2.5}$ concentrations. However, determining pollution
462 levels using total VOCs concentrations are random and unfounded. $PM_{2.5}$ (fine particulate matter
463 with a diameter of less than 2.5 μm) is the premier pollutant of atmosphere pollution in winter in
464 NCP and $PM_{2.5}$ pollution grading standards is clear and specific in the Air Quality Index (AQI)
465 technical regulations (HJ 633-2012) formulated by the Chinese Ministry of Environmental
466 Protection. In view of the above-mentioned facts, in this study, drawing on the $PM_{2.5}$ concentrations
467 as a reference and considering the quantity of samples analyzed, days with average concentrations
468 of $PM_{2.5}$ <75, 75≤$PM_{2.5}$ <150, and $PM_{2.5}$ ≥150 μg m^{-3} were defined as clean (C), moderate pollution
469 (MP), and heavy pollution (HP) days, respectively. $PM_{2.5}$ was measured continuously using
470 RP1400-$PM_{2.5}$ instruments at the Xianghe site. The time series of the $PM_{2.5}$ concentrations during
471 the entire observational period are presented in Figure S5.

472 **3.4.1 Concentration variations at different pollution levels**

473 The mean concentrations and fractional contributions of VOC groups at different pollution
474 levels during the entire observational period are shown in Figure 6a-6b. The statical analysis of the
475 results was performed using IBM SPSS Statistics 22. Seen from Figure 6a, the results showed that
476 there was significant difference of the seven VOC groups at $p<0.01$ at same pollution level. At
477 different pollution levels, there was significant difference of alkanes and alkenes at $p<0.001$, but
478 aromatics, OVOCs, halocarbons and acetonitrile at $p<0.01$, and acetylene at $p<0.05$. The statical
479 analysis suggested that the differences are statistically significant.

480 Figure 6a indicates that nearly all the VOC groups increased continuously and noticeably with
481 the deterioration of the air quality. The mixing ratios of the total VOCs in Xianghe were relatively
482 low on clean days, with an average value of 33.09 ±30.55 ppbv, but increased to 164.12±94.49 ppbv
483 on average on heavy pollution days, among which alkanes were the most abundant chemical groups,
484 accounting for 34.48% (56.59±33.71 ppbv) of the total VOCs. Alkenes and aromatics were two
485 other major components. Their average mixing ratios increased by 576.13% and 485.23%,
486 respectively, on heavy pollution days. Acetylene, which mainly comes from incomplete combustion,
487 and acetonitrile, which is a typical tracer of biomass burning, increased dramatically to 11.67±8.19
488 ppbv and 1.02±1.43 ppbv on average, i.e., by 477.48% and 540.10%, respectively, compared with
489 that on clean days. The fractional contributions of VOC groups to the total VOCs at different
490 pollution levels are presented in Figure 6b. Visibly, the fractional contribution of alkanes decreased
491 from clean days to heavy pollution days, whereas alkenes and aromatics increased and the others
492 remained nearly constant, indicating the significance of alkenes and aromatics in the evolution
493 process of pollution (Guo et al., 2014).

494 Table S1 summarizes the average mixing ratios of all 101 VOC species measured in this
495 campaign. It is evident that the average concentrations of alomost all quantified individual species
496 remarkably increased from clean days to heavy pollution days, and their average concentrations on
497 heavy pollution days were 1-8 times higher than those on clean days, which is in good agreement
498 with previous studies (Zhang et al., 2014; Wu et al., 2016; Liu et al., 2017), except for several
499 halocabons (e.g., CFC-113, 1,4-dichlorobenzene and trichloroethylene), where the mixing ratios
500 remained constant. As each hydrocarbon source has its own characteristic chemical composition,
501 variations in chemical compositions may indicate differences in the source contributions (Wang et

al., 2010). As listed in Table S9, tracers of gasoline vehicle exhaust, diesel vehicle exhaust, petrochemical industry, paint solvent usage, industrial sources and secondary and long-lived species comprised the top 20 most increased species, suggesting the importance of these sources in the evolution of pollution. Of note, among the top 20 VOC species, eight are toxic hydrocarbons, including 1,3-butadiene, styrene, benzene, methylene chloride, 1,2-dichloropropane, chloroform, 1,1,2-trichloroethane and ethylbenzene, as shown in Table S2. This finding suggested a potential health risk to the public on pollution days. Parallel results were observed in October 2014 in Beijing (Wu et al., 2016).

3.4.2 Source contributions at different pollution levels

Figure 6c-6d illustrates the evolution of source factors to the total VOCs mixing ratios at different pollution levels. In order to determine the significance of the difference in relationships to the uncertainties found for the different contributions, we summary the bootstrap calculation (with 100 bootstraps and using a minimum correlation R-value of 0.6) with the variability in the concentrations and percentages of TVOCs for the factors at different pollution levels, as showed in Table S10 and Table S11. For each factor, the median bootstrap value is typically within ±15% of the base run value (Table S10) and the interquartile range of the bootstrap run values is mostly within ±15% of the bootstrap median at different pollution levels (Table S11), showing that the percentages were reasonable. The presences of discrepancies of the concentrations/percentages of base value, BS 5th, BS 25th, BS 50th, BS 75th and BS 95th among factors at different pollution levels, as showed in Table S10 and Table S11, demonstrate that the differences of these contributions are significant. In conclusion, the evolution of mean concentrations and fractional contributions of PMF-derived sources at different pollution levels in this study was reasonable.

As showed in Figure 6c, nearly all of the source mixing ratio contributions increased continuously with the aggravation of pollution. Industrial emissions and vehicle exhaust were the largest contributors to the total VOCs mixing ratios on clean days, but vehicle exhaust and liquefied petroleum gas & natural gas on moderate pollution days, vehicle exhaust, industrial emissions and solvent utilization on heavy pollution days. The fractional contributions of vehicle exhaust and solvent utilization increased continuously over time, whereas the fractional contributions of industrial emissions and secondary and long-lived species decreased continuously, liquefied petroleum gas & natural gas kept constant on clean days and heavy pollution days, as showed in Figure 6d. On clean days, industrial emissions was the largest contributor (30.2%) to the total VOCs mixing ratios, contributing 10.4 ppbv, followed by vehicle exhaustsolvent utilization (8.6 ppbv, 25.0%) and liquefied petroleum gas & natural gas (5.8 ppbv, 16.7%). Solvent utilization and secondary and long-lived species contributed 4.8 and 4.8 ppbv, accounting for 14.0% and 14.0%, respectively, of the total VOCs. On moderate pollution days, the largest contributor was vehicle exhaust, with 30.3 ppbv, accounting for 26.5% of total VOCs, followed by liquefied petroleum gas & natural gas (29.2 ppbv, 25.6%), solvent utilization (20.7 ppbv, 18.1%), secondary and long-lived species (17.7 ppbv, 15.5%) and industrial emissions (16.4 ppbv, 14.3%). On heavy pollution days, the largest contributor was vehicle exhaust, with 59.0 ppbv, accounting for 28.6% of total VOCs. The second largest contributor was industrial emissions (44.8 ppbv, 21.7%) and solvent utilization (44.6 ppbv, 21.6%). The contributions from liquefied petroleum gas & natural gas and secondary and long-lived species were 35.0 ppbv and 22.7 ppbv, accounting for 17.0 and 11.0%, respectively, of the total VOCs. Compared with that on clean days, the contribution of vehicular exhaust increased to the greatest extent, with a value of 50.4 ppbv, followed by solvent utilization (39.7 ppbv) and

546 Industrial emissions (34.4 ppbv).

547 Increases in vehicular exhaust and solvent utilization, industrial emissions, liquefied petroleum
548 gas & natural gas and secondary and long-lived species were responsible for 29.4, 23.2, 20.0, 17.0
549 and 10.4%, respectively, of the increases in ambient VOCs, indicating that vehicle exhaust, solvent
550 utilization and industrial emissions played a key role in the development of pollution levels in
551 Xianghe. The evidently elevated contributions of vehicle exhaust and solvent utilization can be
552 accounted for by the following facts: 1) Vehicle-related emission was an important source, although
553 more stringent emission standards for new vehicles have been implemented in Beijing-Tianjin-
554 Hebei. As of the end of 2016, the number of vehicles reached 19.22 million, accounting for 32.03%
555 in Beijing-Tianjin-Hebei and its surrounding areas, and the vehicle output in Hebei Province reached
556 1.29 million, with 29.1% in the Jing-Jin-Ji region (http://www.hetj.gov.cn/res/nj2017/indexch.htm).
557 2) Solvent use is a major contributor to the increase in VOC emissions, which is estimated to have
558 increased by 52% since 2010, making solvents the largest contributor (36%) to VOC emissions in
559 2017 in China (Zheng et al., 2018). According to the China Furniture Yearbook, as of the end of
560 2016, the number of brands in Xianghe was as high as 1500. Consequently, emission reductions of
561 vehicle exhaust and solvent usage are the optimal scheme to reduce the mixing ratio of VOCs in
562 Xianghe.

563 **3.4.3 Health risk assessment at different pollution levels**

564 Noncarcinogenic risk assessment results of VOC species at different pollution levels are shown
565 in Figure 7 and Table S12. HI was 2.7, 7.4 and 15.1, respectively, on clean days, moderate pollution
566 days and heavy pollution days, suggesting a increasing noncarcinogenic risk (Table S12) with the
567 aggravation of pollution. Specifically, compared with that on clean days, the HQ of methylene

chloride, 1,3-butadiene, styrene, 1,2-dichloropropane and benzene increased remarkably by a factor of 8.3, 8.2, 7.9, 7.8 and 6.7, respectively, on heavy pollution days. Noticeably, the HQ of acrolein was higher than a safe level (=1) on clean days, posing a clear risk to public health, which should be paid more attention. In contrast, the HI of the other noncarcinogens was lower than a safe level, although it increased gradually with the degradation of air quality.

Carcinogenic risk assessment results of VOC species at different pollution levels are shown in Figure 7 and Table S12. Cumulative cancer risk was 2.8×10^{-5}, 8.3×10^{-5} and 1.5×10^{-4}, respectively, on clean days, moderate pollution days and heavy pollution days, suggesting a increasing cumulative cancer risk (Table S12) with the aggravation of pollution. Cumulative cancer risk estimates on clean days were lower than average estimates in Tianjin and South Baltimore. However, Cumulative cancer risk estimates on moderate pollution days and heavy pollution days were much higher than average estimates in Tianjin and South Baltimore (Payne-Sturges et al., 2004; Zhou et al., 2011). Specifically, the risks of 1,3-butadiene, benzene, chloroform and 1,2-dichloroethane on celan days were above the acceptable level of 1×10^{-6} but below a tolerable risk of 1×10^{-4}, showing a potential carcinogenic risk. The cancer risk of acetaldehyde increased gradually until it exceeded the acceptable level of 1×10^{-6} but below a tolerable risk of 1×10^{-4} on heavy pollution days. Apart from the above-mentioned potentially toxic VOC species, the cancer risks of the others were lower than the acceptable level of 1×10^{-6}, although they increased continuously with the aggravation of pollution.

In addition to the evolution of the noncarcinogenic and carcinogenic risks of VOC species at different pollution levels, significant variations in noncarcinogenic and carcinogenic risks of predicted VOC sources were also observed. As presented in Figure 5c-5d, Table S13 and Table S14,

590 the noncarcinogenic and carcinogenic risks of predicted VOC sources increased noticeably with
591 increasing pollution levels. For the noncarcinogenic risk of predicted sources, as showed in Figure
592 5c and Table S13 ,vehicle exhaust, industrial emissions and secondary and long-lived species
593 eventually exceeded acceptable safe levels during the transitions from clean days to heavy pollution
594 days, whereas the other sources remained lower than safe levels at different pollution levels. For the
595 carcinogenic risk of predicted sources, as showed in Figure 5d and Table S14, all sources eventually
596 exceeded the USEPA acceptable level (1×10^{-6}) but remained lower than the tolerable risk (1×10^{-4}).
597 These findings revealed that predicted sources exerted increasing noncarcinogenic and carcinogenic
598 risks on the public with the evolution of pollution levels.

599 **4 Conclusions**

600 This study represents the first field online observations of VOCs in Xianghe, focusing on
601 concentration levels and sources of ambient VOCs and their associated risk to public health. Over
602 the entire period of the study, the total VOCs varied greatly from 4.61 ppbv to 511.98 ppbv. The
603 most dominant compounds were alkanes, followed by alkenes, aromatics, halocarbons, OVOCs,
604 acetylene and acetonitrile. Source apportionment analysis identified five sources, namely, vehicle
605 exhaust (31.0%), industrial emissions (26.4%), liquefied petroleum gas & natural gas (18.6%),
606 solvent utilization (13.6%)and secondary and long-lived species (10.4%). Health risk assessment
607 screening indicated that the noncarcinogenic risk of acrolein (4.9) exceeded 1.0, and the
608 carcinogenic risks of all selected VOCs were lower than the tolerable risk (1×10^{-4}). Estimated
609 noncarcinogenic risks for all sources were below a safe level (= 1), with vehicle exhaust (56.2%)
610 was the largest contributor to noncarcinogenic risk. Estimated carcinogenic risks for nearly all
611 sources were above the USEPA acceptable level (1×10^{-6}) but below the tolerable risk (1×10^{-4}), with

612 solvent utilization (32.6%) was the largest contributor to carcinogenic risk. With the aggravation of
613 pollution, the fractional contribution of alkenes, aromatics, vehicle exhaust and solvent utilization
614 increased during the transition, indicating the significances of these VOC groups and sources in the
615 evolution process of pollution. The noncarcinogenic risks of vehicle exhaust, industrial emissions
616 and secondary and long-lived species eventually exceeded acceptable safe levels, and the
617 carcinogenic risks of nearly all sources eventually exceeded the USEPA acceptable level (1×10^{-6})
618 but remained lower than the tolerable risk (1×10^{-4}), suggesting predicted sources exerted increasing
619 noncarcinogenic and carcinogenic risks on the public with the evolution of pollution levels. We
620 recommend that the priorities for the control of VOC groups and sources include alkenes, aromatics,
621 vehicle exhaust and solvent utilization because of their larger emissions and health risks in Xianghe.

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